

---

# Contents

---

<b>Preface</b> . . . . .	xi
<b>Notations and Symbols</b> . . . . .	xv
<b>Chapter 1. Phase Transformations of Pure Substances</b> . . . . .	1
1.1. Standard state: standard conditions of a transformation . . . . .	1
1.2. Classification and general properties of phase transformations . . . . .	2
1.2.1. First-order transformations and the Clapeyron relation . . . . .	4
1.2.2. Second-order transformations . . . . .	7
1.3. Liquid–vapor transformations and equilibrium states . . . . .	16
1.3.1. Method of two equations of state, using the Clapeyron equation. . . . .	16
1.3.2. Gibbs energy and fugacity method. . . . .	18
1.3.3. Unique equation of state method . . . . .	19
1.3.4. The region of the critical point and spinodal decomposition . . . . .	21
1.3.5. Microscopic modeling . . . . .	22
1.3.6. Liquid–vapor equilibrium in the presence of an inert gas . . . . .	26
1.4. Solid–vapor transformations and equilibria . . . . .	28
1.4.1. Macroscopic treatment. . . . .	28
1.4.2. Microscopic treatment . . . . .	29
1.5. Transformations and solid–liquid equilibria. . . . .	30
1.5.1. Macroscopic treatment. . . . .	31
1.5.2. Microscopic treatment . . . . .	31

1.6. Diagram for the pure substance and properties of the triple point . . . . .	32
1.7. Allotropic and polymorphic varieties of a solid . . . . .	35
1.7.1. Enantiotropy . . . . .	36
1.7.2. Monotropy . . . . .	39
1.7.3. Transition from enantiotropy to monotropy and vice versa . . . . .	39
1.8. Mesomorphic states . . . . .	40
<b>Chapter 2. Properties of Equilibria Between Binary Phases . . . . .</b>	<b>43</b>
2.1. Classification of equilibria between the phases of binary systems . . . . .	43
2.2. General properties of two-phase binary systems . . . . .	45
2.2.1. Equilibrium conditions for two-phase binary systems . . . . .	45
2.2.2. Conditions of evolution of a two-phase binary system . . . . .	46
2.3. Graphical representation of two-phase binary systems . . . . .	47
2.3.1. Gibbs energy graphs . . . . .	47
2.3.2. Phase diagram in the mono- and bi-phase zones . . . . .	53
2.3.3. Isobaric cooling curves . . . . .	63
2.4. Isobaric representation of three-phase binary systems . . . . .	66
2.4.1. Gibbs energy curve . . . . .	66
2.4.2. Isobaric phase diagram in tri-phase regions . . . . .	68
2.4.3. Isobaric cooling curves with tri-phase zones . . . . .	70
2.5. Isothermal phase diagrams . . . . .	72
2.6. Composition/composition curves . . . . .	73
2.7. Activity of the components and consequences of Raoult's and Henry's laws . . . . .	73
<b>Chapter 3. Equilibria Between Binary Condensed Phases . . . . .</b>	<b>75</b>
3.1. Equilibria between phases of the same nature: liquid–liquid or solid–solid . . . . .	76
3.1.1. Thermodynamics of demixing . . . . .	76
3.1.2. Demixing in the case of low reciprocal solubilities . . . . .	79
3.1.3. Demixing of strictly-regular solutions . . . . .	81
3.2. Liquid–solid systems . . . . .	84

---

3.2.1. Thermodynamics of the equilibria between a liquid phase and a solid phase . . . . .	86
3.2.2. Isobaric phase diagrams of equilibria between a solid and a liquid . . . . .	90
3.2.3. Solidus and liquidus in the vicinity of the pure substance. . . . .	97
3.3. Equilibria between two solids with two polymorphic varieties of the solid . . . . .	100
3.4. Applications of solid–liquid equilibria . . . . .	102
3.4.1. Solubility of a solid in a liquid: Schröder–Le Châtelier law . . . . .	102
3.4.2. Determination of molar mass by cryometry . . . . .	104
3.5. Membrane equilibria – osmotic pressure . . . . .	106
3.5.1. Thermodynamics of osmotic pressure. . . . .	107
3.5.2. Osmotic pressure of infinitely-dilute solutions: the Van ‘t Hoff law . . . . .	109
3.5.3. Application of osmotic pressure to the determination of the molar mass of polymers. . . . .	110
3.5.4. Osmotic pressure of strictly-regular solutions . . . . .	111
3.5.5. Osmotic pressure and the osmotic coefficient . . . . .	112
<b>Chapter 4. Equilibria Between Binary Fluid Phases . . . . .</b>	<b>113</b>
4.1. Thermodynamics of liquid–vapor equilibrium in a binary system . . . . .	113
4.2. Liquid–vapor equilibrium in perfect solutions far from the critical conditions . . . . .	117
4.2.1. Partial pressures and total pressure of a perfect solution . . . . .	118
4.2.2. Isothermal diagram of a perfect solution . . . . .	119
4.2.3. Isobaric diagram of a perfect solution . . . . .	120
4.2.4. Phase composition curve . . . . .	121
4.3. Liquid–gas equilibria in ideal dilute solutions . . . . .	122
4.4. Diagrams of the liquid–vapor equilibria in real solutions . . . . .	125
4.4.1. Total miscibility in the liquid phase . . . . .	125
4.4.2. Partial miscibility in the liquid phase, heteroazeotropes . . . . .	128
4.5. Thermodynamics of liquid–vapor azeotropy . . . . .	129
4.5.1. Relation between the pressure of the azeotrope and the activity coefficients of the liquid phase at the azeotropic composition . . . . .	129

4.5.2. Relation between the activity coefficient and the temperature of the azeotrope . . . . .	130
4.6. Liquid–vapor equilibria and models of solutions . . . . .	132
4.6.1. Liquid–vapor equilibria in strictly-regular solutions . . . . .	132
4.6.2. Liquid–vapor equilibrium in associated solutions . . . . .	137
4.7. Liquid–vapor equilibria in the critical region . . . . .	140
4.8. Applications of liquid–vapor equilibria . . . . .	143
4.8.1. Solubility of a gas in a liquid . . . . .	143
4.8.2. Determination of molar masses by tonometry . . . . .	145
4.8.3. Determination of molar masses by ebulliometry . . . . .	146
4.8.4. Continuous rectification or fractional distillation . . . . .	149
<b>Chapter 5. Equilibria Between Ternary Fluid Phases . . . . .</b>	<b>163</b>
5.1. Representation of the composition of ternary systems . . . . .	163
5.1.1. Symmetrical representation of the Gibbs triangle . . . . .	163
5.1.2. Dissymmetrical representation of the right triangle . . . . .	168
5.2. Representation of phase equilibria . . . . .	169
5.2.1. Isothermal projections . . . . .	169
5.2.2. Conjugate points and conodes . . . . .	170
5.2.3. Isoleth sections . . . . .	171
5.3. Equilibria in liquid phases with miscibility gaps . . . . .	171
5.3.1. Representation of the miscibility gap . . . . .	171
5.3.2. Sharing in liquid–liquid systems . . . . .	173
5.3.3. Application of sharing between two liquids to solvent extraction . . . . .	177
5.4. Liquid–vapor systems . . . . .	182
5.4.1. Isothermal and isopleth sections (boiling and dew) . . . . .	182
5.4.2. Distillation trajectories . . . . .	184
5.4.3. Systems with two distillation fields . . . . .	186
5.4.4. Systems with three distillation fields . . . . .	187
5.5. Examples of applications of ternary diagrams between fluid phases . . . . .	187
5.5.1. Treatment of argentiferous lead . . . . .	187
5.5.2. Purity of oil products: aniline point . . . . .	188
5.5.3. Obtaining concentrated ethyl alcohol . . . . .	189
<b>Chapter 6. Equilibria Between Condensed Ternary Fluid Phases . . . . .</b>	<b>191</b>
6.1. Solidification of a ternary system with total miscibility in the liquid state and in the solid state . . . . .	192
6.2. Solidification of a ternary system with no miscibility and with a ternary eutectic . . . . .	192

---

6.2.1. Invariant transformations of a liquid–solid ternary system . . . . .	193
6.2.2. Representations of the ternary system with no miscibility in the solid state. . . . .	194
6.2.3. Lowering of the melting point of a binary system by the addition of a component. . . . .	199
6.2.4. Slope at the ternary eutectic. . . . .	202
6.3. Ternary systems with partial miscibilities in the solid state and ternary eutectic . . . . .	204
6.4. Solidification of ternary systems with definite compounds. . . . .	208
6.4.1. Ternary system with a binary definite compound binary with congruent melting . . . . .	208
6.4.2. Generalization to the case of a ternary compound and of multiple definite compounds. . . . .	211
6.4.3. Definite compound with incongruent melting: quasi-peritectic transformation . . . . .	213
6.5. A peritectic transformation in one binary system and total miscibility in the other two . . . . .	215
6.6. The ternary peritectic transformation. . . . .	217
<b>Bibliography</b> . . . . .	219
<b>Index</b> . . . . .	221